

Emerging Contaminants – Perfluorooctane Sulfonate (PFOS) and Perfluorooctanoic Acid (PFOA)

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EMERGING CONTAMINANTS FACT SHEET – PFOS and PFOA

At a Glance

- ❖ Fully fluorinated compounds that are human-made substances and not naturally found in the environment.
- ❖ Used as a surface-active agent and in variety of products, such as fire fighting foams, coating additives, and cleaning products.
- ❖ Do not hydrolyze, photolyze, or biodegrade under typical environmental conditions and are extremely persistent in the environment.
- ❖ Studies have shown they have the potential to bioaccumulate and biomagnify in wildlife.
- ❖ Readily absorbed after oral exposure and accumulates primarily in the serum, kidney, and liver.
- ❖ Toxicological studies on animals indicate potential developmental, reproductive, and systemic effects.
- ❖ Health-based advisories or screening levels for PFOS and PFOA have been developed by both the EPA and the states agencies.
- ❖ Standard detection methods include high-performance liquid chromatography and tandem mass spectrometry (MS/MS).
- ❖ Common water treatment technologies include activated carbon filters and reverse osmosis units.

Introduction

An “emerging contaminant” is a chemical or material that is characterized by a perceived, potential or real threat to human health or the environment or by a lack of published health standards. A contaminant may also be “emerging” because a new source or a new pathway to humans has been discovered or a new detection method or treatment technology has been developed (DoD 2011). This fact sheet, developed by the U.S. Environmental Protection Agency’s Federal Facilities Restoration and Reuse Office (FFRRO), provides a brief summary of the emerging contaminants perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), including physical and chemical properties; environmental and health impacts; existing federal and state guidelines; detection and treatment methods; and additional sources of information.

PFOS and PFOA are extremely persistent in the environment and resistant to typical environmental degradation processes. As a result, they are widely distributed across the higher trophic levels and are found in soil, air, and groundwater at sites across the United States. The toxicity and bioaccumulation potential of PFOS and PFOA indicate a cause of concern for the environment and human health. This fact sheet is intended for use by site managers faced with addressing PFOS and PFOA at cleanup sites or in drinking water supplies and for those in a position to consider whether these chemicals should be added to the analytical suite for site investigations.

What are PFOS and PFOA?

- ❖ PFOS and PFOA are fully fluorinated, organic compounds and are the two perfluorinated chemicals (PFCs) made in the largest amounts within the United States (ATSDR 2009).
- ❖ PFOS is a perfluoralkyl sulfonate that is commonly used as a simple salt (such as potassium, sodium, or ammonium) or incorporated into larger polymers (EFSA 2008; EPA 2009b).
- ❖ PFOA is a perfluoralkyl carboxylate that is produced synthetically as its salts. Ammonium salt is the most widely produced form (EFSA 2008; EPA 2009b).
- ❖ PFOS synonyms include 1-octanesulfonic acid, 1-octanesulfonic acid, heptadecafluoro-, 1-perfluorooctanesulfonic acid, heptadecafluoro-1-octanesulfonic acid, perfluoro-n-octanesulfonic acid, perfluorooctanesulfonic acid, and perfluorooctylsulfonic acid (ATSDR 2009; UNEP 2005).
- ❖ PFOA synonyms include pentadecafluoro-1-octanoic acid, pentadecafluoro-n-octanoic acid, pentadecafluorooctanoic acid, perfluorocaprylic acid, perfluorooctanoic acid, perfluoroheptanecarboxylic acid, and octanoic acid (ATSDR 2009).

What are PFOS and PFOA? (continued)

- ❖ They are stable chemicals made of a long carbon chain that is both lipid- and water-repellent. Because of the unique amphiphilic character, PFOS and PFOA are used as surface-active agents in various high-temperature applications and for applications in contact with strong acids or bases (ATSDR 2009; UNEP 2005).
- ❖ They are used in a wide variety of industrial and commercial products such as textiles and leather products, fire fighting foams, metal plating, the photographic industry, photolithography, semi-conductors, paper and packaging, coating additives, cleaning products, and pesticides (ATSDR 2009; EPA 2009b; OECD 2002).
- ❖ They are human-made compounds and do not naturally occur in the environment (ATSDR 2009; EPA 2009b).
- ❖ PFOS and PFOA can be formed by environmental microbial degradation or by metabolism in larger organisms from a large group of related substances or precursor compounds (ATSDR 2009; Condor et al. 2010; UNEP 2006).
- ❖ The 3M Company, the primary manufacturer of PFOS, completed a voluntary phase-out of PFOS production in 2002 (ATSDR 2009; EPA 2009b).
- ❖ PFOS chemicals are no longer manufactured in United States. However, they can be imported and used for specific limited uses (EPA 2009b).
- ❖ PFOA is primarily manufactured for use as an aqueous dispersion agent, as ammonium salt, in the manufacture of fluoropolymers, which are used in a wide variety of mechanical and industrial components. They are also produced unintentionally by the degradation of some fluorotelomers (EPA 2009b).
- ❖ As part of the EPA's PFOA stewardship program, eight companies committed to reduce global facility emissions and product content of PFOA and related chemicals by 95 percent by 2010, and to work toward elimination of emissions and product content by 2015 (ATSDR 2009; EPA 2013).

Exhibit 1: Physical and Chemical Properties of PFOS and PFOA

(ATSDR 2009; Brooke et al. 2004; Cheng et al. 2008; EFSA 2008; Environment Canada 2012; EPA 2002b; OECD 2002; UNEP 2006)

Property	PFOS (Potassium Salt)	PFOA
CAS Number	2795-39-3	335-67-1
Physical Description (physical state at room temperature and atmospheric pressure)	White Powder	White powder/waxy white solid
Molecular weight (g/mol)	538 (potassium salt)	414
Water solubility (mg/L at 25°C)	570 (purified), 370 (freshwater), 25 (filtered seawater)	9.5 X 10 ³ (purified)
Melting Point (°C)	> 400	45 to 50
Boiling point (°C)	Not measurable	188
Vapor pressure at 20 °C (mm Hg)	2.48 X10 ⁻⁶	0.017
Air water partition coefficient (Pa.m ³ /mol)	< 2 X10 ⁻⁶	Not available
Octanol-water partition coefficient (log K _{ow})	Not measurable	Not measurable
Organic-carbon partition coefficient (log K _{oc})	2.57	2.06
Henry's law constant (atm m ³ /mol)	3.05 × 10 ⁻⁹	Not measurable
Half-Life	Atmospheric: 114 days Water: > 41 years (at 25° C)	Atmospheric: 90 days* Water: > 92 years (at 25° C)

Notes: g/mol – grams per mole; mg/L – milligrams per liter; °C – degree Celsius; mm Hg – millimeters of mercury; Pa m³/mol – pascal-cubic meters per mole; atm m³/mol – atmosphere-cubic meters per mole.

* The identified atmospheric half-life value for PFOA is estimated based on available data determined from short study periods.

What are the environmental impacts of PFOS and PFOA?

- ❖ During past manufacturing processes, large amounts of PFOS and PFOA were released to the air, water, and soil in and around fluorochemical facilities (ATSDR 2009).
- ❖ PFOS and PFOA have been detected in a number of U.S. cities in surface water and sediments downstream of former production facilities, wastewater treatment plant effluent, sewage sludge, and landfill leachate (EPA 2002b; OECD 2002).
- ❖ Both PFOS and PFOA are the stable end products resulting from the degradation of precursor substances through a variety of abiotic and biotic transformation pathways (Conder et al. 2010).
- ❖ PFCs, including PFOS and PFOA, are chemically and biologically stable in the environment and resistant to biodegradation, atmospheric photooxidation, direct photolysis, and hydrolysis. As a result, these chemicals are extremely persistent in the environment (ATSDR 2009).
- ❖ Low acid dissociation constants (pKa) ranging from -3 to 4 suggest that PFOS and PFOA are strong acids and exist predominately in the anionic form in the environment (Conder et al. 2010).
- ❖ When released directly to the atmosphere, PFCs are expected to adsorb to particles and settle onto soil through wet or dry deposition (ATSDR 2009).
- ❖ PFOA and PFOS in anionic form are water-soluble and can migrate readily from soil to groundwater (Conder et al. 2010; Post et al. 2012).
- ❖ As a result of their chemical stability and low volatility in ionic form, PFCs are persistent in water and soil (ATSDR 2009).
- ❖ Monitoring data from the Arctic region and at sites remote from known point sources, have shown highly elevated levels of PFOS and PFOA in environmental media and biota, indicating that long-range transport has occurred (ATSDR 2009; Post et al. 2012; UNEP 2007).
- ❖ Long-range PFC transport sources include the atmospheric transport of precursor compounds, such as perfluoroalkyl sulfonamides, followed by photooxidation to form PFCs, and the direct long-range transport of PFCs via ocean current or in the form of marine aerosols (ATSDR 2009; Post et al. 2012).
- ❖ The wide distribution of PFCs in high trophic levels increases the potential for bioaccumulation and bioconcentration. Because of their persistence and long-term accumulation, higher trophic level wildlife such as fish, piscivorous birds, and Arctic biota can continue to be exposed to PFOS and PFOA (EPA 2006; UNEP 2006).
- ❖ PFOS exhibits a higher tendency to bind to organic matter and bioaccumulate compared to PFOA due to its longer perfluoroalkyl chain length (Conder et al. 2010).
- ❖ PFOS has been shown to bioaccumulate and biomagnify in wildlife species such as fish and piscivorous birds. The biomagnification factor ranges from 1.4 to 17 kilogram per kilogram (kg/kg) in predatory birds and mammals (Moermond et al. 2010; UNEP 2006).
- ❖ PFOS is the only PFC that has been shown to accumulate to levels of concern in fish tissue. The estimated kinetic bioconcentration factor in fish ranges from 1,000 to 4,000 (EFSA 2008; MDH 2011).
- ❖ High levels of PFCs, including PFOA and PFOS, have been reported at both the Oakdale Dump Superfund Site in Oakdale, Minnesota (MN) and Washington County Landfill Site in Lake Elmo, MN (EPA 2012 b, c).

What are the health effects of PFOS and PFOA?

- ❖ Studies have found small quantities of PFOS and PFOA in the blood samples of the general human population and wildlife nationwide, indicating that exposure to the chemicals is widespread (ATSDR 2009; EPA 2006).
- ❖ Data indicate that PFOS and PFOA serum concentrations are higher in workers and individuals living near fluorochemical facilities than those reported for the general population (ATSDR 2009; EPA 2009b).
- ❖ Potential pathways, which may lead to widespread exposure, include ingestion of food and water, use of commercial products, or inhalation from long-range air transport (ATSDR 2009; EPA 2009b; MDH 2011).
- ❖ Based on the limited information available, fish and fishery products seem to be one of the primary sources of human exposure to PFOS. The maximum permissible concentration (MPC) for PFOS, based on consumption of fish by humans as the most critical route, is 0.65 nanograms per liter (ng/L) for freshwater (Moermond et al. 2010).

What are the health effects of PFOS and PFOA? (continued)

- ❖ Studies also indicate that continued exposure to low levels of PFOA in drinking water may result in adverse health effects (Post et al. 2012).
- ❖ Toxicology studies show that PFOS and PFOA are readily absorbed after oral exposure and accumulate primarily in the serum, kidney, and liver. No further metabolism is expected (EFSA 2008; EPA 2006; EPA 2009b).
- ❖ PFOS and PFOA have a long half-life of about 4 years in humans. This continued exposure could increase body burdens to levels that would result in adverse outcomes (ATSDR 2009; EPA 2009b).
- ❖ Acute- and intermediate- duration oral studies in rodents have raised concerns about potential developmental, reproductive, and other systemic effects of PFOS and PFOA (Austin et al. 2003; ATSDR 2009; EPA 2006).
- ❖ The ingestion of PFOA-contaminated water was found to cause adverse effects on mammary gland development in mice (Post et al. 2012).
- ❖ Results of a study indicate that exposure to PFOS can affect the neuroendocrine system in rats (Austin et al. 2003).
- ❖ Both PFOS and PFOA have a high affinity for binding to B-lipoproteins and liver fatty acid-binding protein. Several studies have shown that these compounds can interfere with fatty acid metabolism and may deregulate metabolism of lipids and lipoproteins (EFSA 2008; EPA 2009b).
- ❖ The EPA Science Advisory Board suggested that PFOA cancer data are consistent with the EPA guidelines for the Carcinogen Risk Assessment descriptor “likely to be carcinogenic to humans”. EPA is still in the process of evaluating this information and additional research pertaining to the carcinogenicity of PFOA (EPA 2013).
- ❖ The EPA has not derived a reference dose (RfD) or reference concentration (RfC) for PFOS or PFOA and has not classified PFOS or PFOA as to their carcinogenicity (ATSDR 2009).
- ❖ The American Conference of Industrial Hygienists (ACGIH) has classified PFOA as a Group A3 confirmed animal carcinogen with unknown relevance to humans (ACGIH 2002).
- ❖ The chronic exposure to PFOS and PFOA can lead to the development of tumors in the liver of rats; however, more research is needed to determine if there are similar cancer risks for humans (ATSDR 2009; OECD 2002).
- ❖ In a retrospective cohort mortality study of over 6,000 PFOA-exposed employees, results identified elevated standardized mortality ratios for kidney cancer and a statistically significant increase in diabetes mortality for male workers at the plant. The study noted that additional investigations are needed to confirm these findings (DuPont 2006; Lau et al. 2007).
- ❖ Studies have shown that PFCs may induce modest effects on reactive oxygen species and deoxyribonucleic acid (DNA) damage in the cells of the human liver (Eriksen et al. 2010).
- ❖ Analysis of U.S. National Health and Nutrition Examination Survey representative study samples indicate that higher concentrations of serum PFOA and PFOS are associated with thyroid disease in the U.S. general adult population; however, further analysis is needed to identify the mechanisms underlying this association (Melzer et al. 2010).
- ❖ Epidemiologic studies have shown an association between PFOS exposure and bladder cancer; however, further research is needed (EPA 2006; OECD 2002).
- ❖ The EPA removed PFOS and PFOA from the Integrated Risk Information System (IRIS) agenda in a Federal Register Notice released on October 18, 2010. At this time, EPA is not conducting an IRIS assessment for these chemicals (EPA 2010).

Are there any federal and state guidelines and health standards for PFOS and PFOA?

- ❖ The Agency for Toxic Substances and Disease Registry has not established a minimal risk level (MRL) for PFOS or PFOA because human studies were insufficient at the time the draft toxicological profile was published to determine with a sufficient degree of certainty that the effects are either exposure-related or adverse (ATSDR 2009).
- ❖ The EPA finalized two Significant New Use Rules (SNURs) in 2002, requiring companies to inform the EPA 90 days before they manufacture or import 88 identified PFOS-related substances (EPA 2002a; UNEP 2006).

Are there any federal and state guidelines and health standards for PFOS and PFOA? (continued)

- ❖ In 2007, the SNURs were amended to include 183 additional PFOS-related substances with carbon chain lengths of five carbons and higher (EPA 2006).
- ❖ Under the Toxic Substances Control Act (TSCA), EPA proposed a SNUR in August 2012 requiring companies to report 90 days in advance of all new uses of long-chain perfluoroalkyl carboxylic (LCPFAC) chemicals for use as part of carpets or to treat carpets, including the import of new carpet containing LCPFACs. The EPA is also proposing to amend the existing SNUR to add 7 additional PFOS-related substances and add “processing” in the definition of significant new use (EPA 2012a; EPA 2013).
- ❖ The SNURs allow for the continuation of a few limited, highly technical uses of PFOS where there are no alternatives available, and which are characterized by very low volume, low exposure, and low releases (ATSDR 2009; EPA 2006).
- ❖ In January 2009, the EPA’s Office of Water established a provisional health advisory (PHA) of 0.2 micrograms per liter (µg/L) for PFOS and 0.4 µg/L for PFOA to protect against the potential risk from short-term exposure of these chemicals through drinking water (EPA 2009c; EPA 2013).
- ❖ EPA Region 4 recommended a residential soil screening level of 6 milligrams per kilogram (mg/kg) for PFOS and 16 mg/kg for PFOA (EPA 2009d).
- ❖ Minnesota has established a health risk limit of 0.3 µg/L for PFOS and PFOA in drinking water (MDH 2011).
- ❖ New Jersey has established a preliminary health-based guidance value of 0.04 µg/L for PFOA in drinking water (NJDEP 2007).
- ❖ North Carolina has established an interim maximum allowable concentration of 2 µg/L for PFOA in ground water (NCDENP 2008).

What detection and site characterization methods are available for PFOS and PFOA?

- ❖ Detection methods for environmental samples are primarily based on high-performance liquid chromatography (HPLC) coupled with tandem mass spectrometry (MS/MS) (ATSDR 2009).
- ❖ HPLC-MS/MS has allowed for more sensitive determination of individual PFOS and PFOA in air, water, and soil (ATSDR 2009).
- ❖ Both liquid chromatography (LC)-MS/MS and gas chromatography-mass spectrometry (GC-MS) can be used to identify the precursors of PFOS and PFOA (EFSA 2008).
- ❖ EPA Method 537, Version 1.1 is a LC-MS/MS method used for the determination of selected perfluorinated alkyl acids in drinking water (EPA 2009a). It may also be used to analyze groundwater samples for PFOA.
- ❖ The development of LC – electrospray ionization (ESI) MS and LC-MS/MS has improved the analysis of PFOS and PFOA (EFSA 2008).
- ❖ Sample preparation methods include solvent extraction, ion-pair extraction, solid-phase extraction, and column-switching extraction (ATSDR 2009).
- ❖ Air samples may be collected using high-volume air samplers that employ sampling modules containing glass-fiber filters and glass columns with a polyurethane foam (EFSA 2008).
- ❖ Reported sensitivities for the available detection methods include low picograms per cubic meter (pg/m³) levels in air, high picograms per liter (pg/L) to low nanograms per liter (ng/L) levels in water, and high picogram per gram (pg/g) to low nanogram per gram (ng/g) levels in soil (ATSDR 2009).

What technologies are being used to treat PFOS and PFOA?

- ❖ Because of their unique physiochemical properties (strong fluorine-carbon bond and low vapor pressure), PFOS and PFOA resist most conventional treatment technologies such as direct oxidation and biodegradation (Hartten 2009; Vectis et al. 2009).
- ❖ The optimal treatment method depends on the concentration of PFOS and PFOA, background organic and metal concentration, available degradation time, and other site-specific conditions (Vectis et al. 2009).
- ❖ Both activated carbon filters and reverse osmosis units have been shown to be effective at reducing PFCs in water at levels typically found in drinking water; however, incineration of the concentrated waste is required for complete destruction of PFOS and PFOA (Hartten 2009; MDH 2008; Vectis et al. 2009).
- ❖ Alternative technologies studied for PFOS and PFOA degradation include photochemical oxidation and thermally-induced reduction (Hartten 2009; Vectis et al. 2009).
- ❖ Studies have also evaluated the use of sonochemical degradation to treat PFOS and PFOA in groundwater (Cheng et al. 2008; Vectis et al. 2009).

Where can I find more information about PFOS and PFOA?

- ❖ American Conference of Governmental Industrial Hygienists (ACGIH). 2002. Documentation of the threshold limit values and biological exposure indices. Cincinnati, Ohio.
- ❖ Agency for Toxic Substance and Disease Registry (ATSDR). 2009. "Draft Toxicological Profile for Perfluoroalkyls." www.atsdr.cdc.gov/toxprofiles/tp200.pdf
- ❖ Austin, M.E., Kasturi, B.S., Barber, M., Kannan, K., MohanKumar, P.S., and MohanKumar, S.M. 2003. "Neuroendocrine effects of perfluorooctane sulfonate in rats." *Environmental Health Perspectives*. Volume 111(12). Pages 1485 to 1489. www.ncbi.nlm.nih.gov/pmc/articles/PMC1241651/
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- ❖ Conder, J.M., Wenning, R.J., Travers, M., and Blom, M. 2010. "Overview of the Environmental Fate of Perfluorinated Compounds." Network for Industrially Contaminated Land in Europe (NICOLE) Technical Meeting. 4 November 2010.
- ❖ DuPont. 2006. Ammonium perfluorooctanoate: Phase II. "Retrospective cohort mortality analyses related to a serum biomarker of exposure in a polymer production plant."
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- ❖ European Food Safety Authority (EFSA). 2008. "Perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA) and their salts." *The EFSA Journal*. Volume 6 (53). Pages 1 to 131.
- ❖ Hartten, A.S. 2009. "Water Treatment of PFOA and PFOS." DuPont Corporate Remediation Group. www.epa.gov/oppt/pfoa/pubs/Water%20Treatment%20Methods%20Hartten%20Oct16-09.pdf
- ❖ Lau, C., Anitole, K., Hodes, C., Lai, D., Pfahles-Hutchens, A., and Seed, J. 2007. "Perfluoroalkyl Acids: A Review of Monitoring and Toxicological Findings." *Toxicological Sciences*. Volume 99 (2). Pages 366 to 394.
- ❖ Melzer, D., Rice, N., Depledge, M.H., Henley, W.F., and Galloway, T.S. 2010. "Association between Serum Perfluorooctanoic Acid (PFOA) and Thyroid Disease in the U.S. National Health and Nutrition Examination Survey." *Environmental Health Perspectives*. Volume 118 (5). Pages 686 to 692. <http://www.ncbi.nlm.nih.gov/pubmed/20089479>
- ❖ Minnesota Department of Health (MDH). 2008. "MDH Evaluation of Point-of-Use Water Treatment Devices for Perfluorochemical Removal. Final Report Summary." www.health.state.mn.us/divs/eh/wells/waterquality/poudevicefinalsummary.pdf

Where can I find more information about PFOS and PFOA? (continued)

- ❖ MDH. 2011. Perfluorochemicals (PFCs) in Minnesota.
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- ❖ New Jersey Department of Environmental Protection (NJDEP). 2007. "Guidance for PFOA in Drinking Water at Pennsgrove Water Supply Company."
http://www.nj.gov/dep/watersupply/pdf/pfoa_dwguidance.pdf
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- ❖ Organization for Economic Cooperation and Development (OECD). Environment Directorate. 2002. "Hazard Assessment of Perfluorooctane Sulfonate (PFOS) and its Salts."
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- ❖ United Nations Environment Programme (UNEP). 2005. "Perfluorooctane sulfonate proposal." Stockholm Convention on Persistent Organic Pollutants Review Committee. Geneva, 7-11 November 2005.
- ❖ UNEP. 2006. "Risk profile on perfluorooctane sulfonate." Stockholm Convention on Persistent Organic Pollutants Review Committee. Geneva, 21 November 2006.
- ❖ UNEP. 2007. "Risk Management Evaluation on Perfluorooctane Sulfonate." Stockholm Convention on Persistent Organic Pollutants Review Committee. Geneva, 19-23 2007.
- ❖ U.S. Department of Defense (DoD). 2011. Emerging Chemical & Material Risks.
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- ❖ EPA. 2009c. "Provisional Health Advisories for Perfluorooctanoic Acid (PFOA) and Perfluorooctyl Sulfonate (PFOS)."
- ❖ EPA Region 4. 2009d. "Soil Screening Levels for Perfluorooctanoic Acid (PFOA) and Perfluorooctyl Sulfonate (PFOS)." Memorandum.
- ❖ EPA. 2010. "Integrated Risk Information System (IRIS); Request for Chemical Substance Nominations for the 2011 Program." Federal Register Notice. Volume 75 (200). Pages 63827 to 63830.
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- ❖ EPA 2012a. "Perfluoroalkyl Sulfonates and Long-Chain Perfluoroalkyl Carboxylate Chemical Substances; Proposed Significant New Use Rule." Code of Federal Regulations. 40 CFR 721.
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- ❖ EPA. 2012c. "Superfund Site Progress Profile: Washington County Landfill." Superfund Information Systems.
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